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(54) Title
REMOVAL OF ARSENIC AND ANTIMONY FROM SULPHIDE ORES
CONTAINING NOBLE METALS

(57) Claim

1. A hydrometallurgical method for treating a sulfide ore containing arsenic and antimony to produce an insoluble, disposable solid waste containing all of the As and Sb without creating any toxic, hazardous, or environmentally sensitive solids, liquids, or gases during the treatment, comprising the steps of:

reacting a slurry of the ore with a calcium compound selected from the group consisting of calcium oxide, calcium carbonate, calcium chloride, calcium oxide/calcium carbonate, or mixtures thereof with sufficient oxygen at an elevated temperature and pressure to form an insoluble calcium arsenate complex and antimony oxide solids.

2. The method of claim 1 wherein the reaction occurs at a temperature of between about 90 - 103 C.

3. The method of claim 1 wherein the reaction occurs at a pressure of about 50 - 70 psi.

COMPLETE SPECIFICATION

(ORIGINAL)

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Complete Specification for the invention entitled:

METHOD OF TREATING ARSENIC SULFIDE ORES

The following statement is a full description of this invention, including the best method of performing it known to :-

METHOD OF TREATING ARSENIC SULFIDE ORES

TECHNICAL FIELD

The present invention relates to a method for treating arsenic, particularly in arsenic sulfide ores containing noble metals, to create an environmentally safe form of arsenic while extracting the desired metal values without formation of intermediate arsenic compounds that are toxic.

BACKGROUND ART

Arsenic can be one of the most toxic chemicals, yet it is relatively abundant in safe forms in sulfide ores, particularly in the Western United States, Canada, Alaska, and South Africa where the ores contain noble metals, such as gold silver, and cobalt, which are valuable precious metals. Recovery of these metal values, which appear in low grade amounts, generally, has been problematic, because the known smelting and hydrometallurgical methods for treating these ores generate toxic arsenic intermediates or generate waste products containing arsenic which are toxic, hazardous, or environmentally sensitive. For this reason, the Asarco smelter in Tacoma, Washington will soon be closing, since the emission standards placed upon its flue exhaust makes it uneconomical to treat arsenic sulfide ores to recover gold and silver. With the closing of the Asarco smelter, there will be no commercial operations in the United States or Canada processing arsenic sulfide ores.

In my copending patent application, U.S.S.N. 607,010, I describe a hydrometallurgical process for the recovery of noble metal values from arsenic sulfide ores. The method entails balancing the combined molar content of arsenic and antimony in the ore(s) being treated with the other metal content of the reaction slurry to allow recovery of the noble metal values without the creation of any environmentally sensitive or toxic arsenic or antimony compounds. This method is an improvement of the method of Smyres, as described in United States patent 4,410,496 which processes complex sulfide ores in the presence of oxygen and

excess calcium chloride to recover noble metal values.

In continuing my research for a commercial process to recover noble metal values from arsenic sulfide ores, I have discovered that I can reduce arsenic and antimony to insoluble, nontoxic, and environmentally safe solid wastes without the formation of any toxic solids, liquids, or gases. This improved and generalised process is the subject of the present invention.

SUMMARY OF THE INVENTION

Environmentally-safe As and Sb solids can be formed in arsenic/antimony containing sulfide ores by reacting the As with CaO , CaCO_3 , or mixtures thereof (with or without calcium chloride in balanced reaction conditions as taught in my earlier application U.S.S.N. 607,010) to produce calcium arsenate complexes while allowing the reaction solids to be leached with cyanide to recover desired metal values. The method preferably occurs at pH of no greater than 3.0, at a temperature maintained between about 90-130 C, and at a pressure of between about 50-70 psi. Sufficient calcium should be added to a slurry of the As/Sb ore so that all the As is consumed with the calcium. The reaction occurs in the presence of oxygen, preferably supplied with compressed air rather than with purified oxygen. Antimony forms SbO solids.

BEST MODE FOR CARRYING OUT THE INVENTION

Although arsenic-containing ores cannot be safely treated directly with cyanide to leach metal values from the ores, it is possible with the method of the present invention to complex the arsenic and antimony into insoluble, nontoxic, nonhazardous solids with a simple process to allow cyanide leaching or other metal recovery processing in a secondary process. In the hydrometallurgical process, CaO , CaCO_3 , or a mixture thereof is added to a slurry of the ore in the presence of oxygen at a temperature maintained between about 90-130C, at a pressure of between about 50-70 psi, and at a pH of no greater than about 3.0 to convert all the antimony to

antimony oxide (SbO) and all the arsenic to a calcium arsenate complex. Toxic, hazardous, or environmentally-sensitive compounds are not formed. The resulting solid can be leached with cyanide to recover the desired metal values, such as silver, gold platinum, and cobalt. Of course, other recovery methods to extract the metal values can be used, if desired, if iron is present in the ore, the complex will be a calcium iron arsenate, which is customarily formed and is preferred. Preferably the raw ore is an arsenic sulfide ore having a major amount of arsenic, and usually at least about 5 wt. % As.

While I have detected the presence of toxic arsenic trichlorides (or suspected their formation) during the calcium chloride processing discussed in the Smyres patent, I believe that the process of this invention could be used on arsenic sulfide ores having at least about 13.65 wt. % arsenic or more simply by adding sufficient CaO , CaCO_3 , or a mixture thereof to consume the entire amount of arsenic into a calcium iron arsenate, which is nontoxic, nonhazardous, and readily disposable in conventional solid waste disposal facilities without special permit from the EPA. As stated above, the process would be carried out in the presence of oxygen at an elevated temperature and pressure. If the calcium is in large excess to the amount of arsenic and antimony in the ore to be treated, it is possible to include calcium chloride along with the limestone or quick lime to provide a chloride carrier for the soluble metal ions that are formed. I prefer to carry out my processing in two steps, however, to ensure that the arsenic and antimony are captured in nonhazardous forms prior to the entry of any compound which could introduce the possibility the production of toxic arsenic or antimony compounds. If I do introduce chloride, I take the precaution of balancing the proportions of arsenic and antimony against the proportions of copper, lead, and zinc in the slurry so that I will not form toxic arsenic or antimony compounds, as taught in my copending application.

As is known to those of ordinary skill in the art, an arsenic sulfide ore is a complex mixture of metal sulfides, including a major amount of AsFeS and very minor amounts of precious metal sulfides. In a hydrometallurgical treatment process, the metals are freed from their sulfides, and become soluble. Because of the toxicity of and danger of soluble arsenic and antimony compounds, particularly AsCl_3 and As_2O_3 , arsenic sulfide ores are not processed with conventional hydrometallurgical processing methods.

Roasting of the arsenic sulfide ores is possible, but significant environmental and health concerns abound with the conventional roasting methods. As previously mentioned, the Asarco smelter in Tacoma, Washington, will be closing due to the environmental restrictions placed upon its emissions. While roasting remains a major processing method in South Africa, recent studies seem to have identified a significant risk associated with the smelter operations. Mine and smelter workers living in close proximity to the smelter appear to have a shortened average life expectancy. I believe that this increased mortality rate is due to the arsenic emissions from the smelting operations.

Until I proposed the hydrometallurgical processing method described in my copending application, there was not a way to safely process arsenic sulfide ores, which are abundant. I have now discovered that the processing of these ores and other forms of arsenic can be safely undertaken by complexing the arsenic into CaFeAs by reacting the solid AsFeS directly with limestone, quick lime, or a mixture thereof without the formation of any toxic, hazardous, or environmentally sensitive arsenic or antimony compounds.

While a preferred embodiment has been described, those skilled in the art will recognise variations, modifications, and alterations which might be made to the embodiment without departing from the incentive concept. The embodiment is meant to illustrate the invention rather than to limit it. The claims should be interpreted

liberally in view of the description to protect the invention, and should not be limited to the preferred embodiment, unless such limitation is necessary in view of the pertinent prior art.

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THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A hydrometallurgical method for treating a sulfide ore containing arsenic and antimony to produce an insoluble, disposable solid waste containing all of the As and Sb without creating any toxic, hazardous, or environmentally sensitive solids, liquids, or gases during the treatment, comprising the steps of:

reacting a slurry of the ore with a calcium compound selected from the group consisting of calcium oxide, calcium carbonate, calcium chloride, calcium oxide/calcium carbonate, or mixtures thereof with sufficient oxygen at an elevated temperature and pressure to form an insoluble calcium arsenate complex and antimony oxide solids.

2. The method of claim 1 wherein the reaction occurs at a temperature of between about 90 - 103 C.

3. The method of claim 1 wherein the reaction occurs at a pressure of about 50 - 70 psi.

4. The method of claim 1 wherein the rate of reaction is increased by allowing the natural acid created in the reaction reduce the pH of the reaction slurry to about 3.0.

5. The method of claim 1 wherein the calcium compound is selected from the group consisting of CaO, CaCO₃, and mixtures thereof.

6. The method of claim 1 wherein the slurry contains iron so that the calcium arsenate complex is a calcium iron arsenate.

7. The method of claim 1 wherein the slurry contains other metal values which are dissolved during the reaction

to allow the separation of the metal values from the arsenic and antimony without the formation of toxic or soluble arsenic or antimony compounds.

8. The method of claim 1 wherein the slurry contains other metal values which are leachable from the solid waste with a conventional cyanide process following creation of the solid arsenic and antimony compounds without the formation of any toxic or soluble arsenic or antimony compounds.

9. The method of claim 8 wherein the reaction occurs at a temperature of between about 90 - 130 C and at a pressure of about 50 - 70 psi.

10. The method of claim 9 wherein the ore contains at least about 5 wt. % arsenic.

11. A hydrometallurgical method for treating arsenic sulfide ores have a major amount of arsenic to separate valuable metal values such as silver and gold from the arsenic and antimony in the ore without producing any toxic, hazardous, or environmentally sensitive arsenic or antimony compounds during the reaction and treatment, comprising the step of:

reacting a slurry of the arsenic sulfide ore with calcium oxide, calcium carbonate, or a mixture thereof in the presence of oxygen at an elevated temperature and pressure, the amount of calcium being at least sufficient to consume all the arsenic in the slurry into insoluble calcium arsenate compounds.

12. The method of claim 11 wherein the reaction occurs at a temperature of between about 90 - 130 C, and at a pressure of about 50 - 70 psi.

13. The method of claim 11 wherein the slurry contains iron and the calcium arsenate solid as a calcium iron arsenate complex.

14. A hydrometallurgical process allowing the cyanide leaching of metal values from arsenic sulfide ores to extract metals values, such as silver and gold, from the ore, the method making arsenic and antimony in the ore into insoluble, nontoxic, disposable, nonhazardous and environmentally safe solids without the formation of any toxic or environmentally safe solids without the formation of any toxic or environmentally sensitive solids, liquids, or gases during the reaction, the method comprising the step of:

adding calcium oxide, calcium carbonate, or a mixture thereof to a slurry of an arsenic sulfide ore containing either arsenic, antimony, or both in the presence of oxygen at a temperature of about 90 - 130 C and at a pressure of about 50 - 70 psi, to produce an arsenic calcium complex and antimony oxide without creating any toxic or environmentally sensitive arsenic or antimony solids, liquids or gases.

15. The method of claim 14 further comprising the step of cyaniding the solid precipitate of the reaction to remove the desired metal values from the solid precipitate while leaving the arsenic and antimony unaffected.

16. The method of claim 15 wherein sufficient calcium is added to consume all the arsenic in the ore into a calcium arsenate complex, wherein the ore contains iron, and wherein the complex is a calcium iron arsenate.

17. The method of claim 15 wherein the ore contains at least about 5 wt. % arsenic.